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Isoconversional methods to determine the kinetics of crude oils - thermogravimetry approach

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ABSTRACT

In this research, kinetics of four crude oils from different origins are determined by iso-conversional methods using thermogravimetry data (TGA-DTG). The experiments were performed at three different heating rates (5-10-15 K/min) between 300 and 1200 K. Thermal characteristics of the crude oil samples such as, reaction intervals and corresponding peak and burn-out temperatures are also determined. Three different iso-conversional methods, known as Starink, Kissinger and Friedman are used in order to determine the activation energy values of the crude oil samples studied that represents the novelty of the research. Activation energy values of the crude oil samples are varied between 50 and 102 kJ/mol and 69–132 kJ/mol in low temperature oxidation region and high temperature oxidation region, respectively.

1. Introduction

Crude oil, commonly known as petroleum is a naturally occurring, unrefined petroleum product composed of hydrocarbon deposits and other organic materials. While hydrocarbons are usually the primary component of crude oil, their composition can vary from 50% to 97% depending on the type of crude oil and how it is extracted.

Thermal analysis techniques are well known approaches to determine the physical and chemical properties of crude oils, as well as kinetics. A better understanding of crude oil characteristics and kinetics using thermal analysis techniques under combustion and pyrolysis conditions is studied by various researchers (Kok, 2003, 2006; Mothe et al., 2013a; Li et al., 2013). Thermogravimetry (TGA) and differential scanning calorimeter (DSC) is mainly used to determine the pyrolysis and combustion properties of crude oils under different atmospheres. In general, two main reaction regions are observed in all the crude oil samples studied, known as low and high temperature oxidation regions, respectively. Reaction intervals, peak and burn-out temperatures, mass loss in each reaction region is also determined for all the crude oil samples studied. Effect of metallic additives, fractions, reservoir rock composition in porous media, pressure, reservoir matrix, reaction rates related to an in-situ combustion (Mothe et al., 2013b; Li et al., 2009; Kok and Iscan, 2012; Kok and Gundogar, 2014). On the other hand, thermal characteristics of heavy oil is studied from the point view of chemical evaluation, kinetics, thermal decomposition, effect of matrix and clay and SARA (saturate, aromatics, resin and asphaltene) fractions (Varfolomeev et al., 2015a, 2015b, 2016a, 2016b, 2016c, 2016d, 2017a, 2017b).

The aim of this research was to study the kinetics of crude oils and determine the activation energy of crude oils using iso-conversional methods non-isothermal thermogravimetric conditions. Starink, Kissinger and Friedman models are used calculate the activation energy of the crude oil samples and to compare the results.

2. Experimental

In this research, combustion characteristics of four crude oil samples of different origin (*Crude oil-1: 12 °API; Crude oil-2: 15 °API; Crude oil-3: 24 °API and Crude oil-4: 31 °API*) is studied using a thermal analysis system (*TA Inst.*) with thermogravimetry (TGA) module, in which mass loss of the samples as a function of temperature is recorded continuously. TGA experiments is performed in the temperature range of 300–1200 K at 5, 10 and 15 K/min heating rates under an air flow rate of 50 ml/min using a sample mass of 10 mg. Prior to experiments, temperature and balance calibrations of the thermogravimetry (TGA) is performed. Reproducibility of the experiments was acceptable and the experimental data presented corresponds to the different operating conditions are the mean values of the runs carried out twice within the experimental error of less than ± 0.25%.

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